

Process and apparatus for recovery of non-ferrous metals from zinc residues

5 This invention relates to the recovery of non-ferrous metals from zinc-bearing residues, in particular from residues produced by the zinc manufacturing industry.

10 Blende, which is an impure ZnS ore, is the main starting material for the production of Zn. The typical industrial practice encompasses an oxidative roasting step, producing ZnO together with sulphates or oxides of the impurities. In subsequent steps, the ZnO in roasted blende is brought into solution by leaching in neutral conditions or in weak acidic conditions, thereby producing Zn-depleted residues, respectively referred to in this description as neutral leach residue and as weak acid leach residue. However, during roasting, part of the Zn reacts with Fe, a typical impurity present in blende, and forms relatively insoluble zinc ferrite. The leach residues therefore contain, besides lead sulphate, calcium sulphate and other impurities, a sizeable fraction of Zn in the form of ferrite.

20 According to present practice, the recovery of the Zn from ferrite requires a specific hydro-metallurgical residue treatment using high acid concentrations of 50 to 200 g/l H₂SO₄. A disadvantage of this acidic treatment is that besides Zn, almost all the Fe and also other impurities such as As, Cu, Cd, Ni, Co, Tl, Sb are dissolved. As even

25 low concentrations of these elements interfere with the subsequent electrowinning of Zn, they must be removed from the zinc sulphate solution. While Cu, Cd, Co, Ni and Tl are precipitated by addition of Zn powder, Fe is typically discarded as hematite, jarosite or goethite through hydrolysis. Due to the danger of washout of heavy

30 metals, these Fe-bearing residues have to be disposed off in a well-controlled landfill. Landfilling of such residues has however come under heavy environmental pressure, rendering the sustainability of the process questionable. Another drawback of the above treatment is the loss of metals such as In, Ge, Ag and Zn in the Fe-bearing

35 residue.

An alternative treatment of the ferrite-bearing residues is applied in some plants, using Waelz kilns, which produce a slag, and a Zn and Pb containing fume. Similarly, a rotary flame-fired furnace of the

40 Dorschel type can be used in a batch process. In still another approach, the leach residue is processed, using coke as fuel, in a half shaft blast furnace, producing a Zn and Pb containing fume,

matte and slag. These pyro-metallurgical treatments generally result in an excellent recovery of Zn and Pb, and, for some of them, in a significant recovery of Ag, Ge and In.

- 5 These processes are however inadequate for modern zinc smelters, as they cannot be scaled up to large single-vessel operations. By this fact, they are not a cost efficient solution for today's Zn smelters.

10 In US 2,932,566 oxidic zinciferous material is smelted with coke in a blast furnace and Zn is recovered from the furnace gases. In an example, fluxes are added to obtain a final slag with 61% FeO, 16% SiO₂, 11.5% CaO and 3% Al₂O₃. In US 4,072,503 Zn-, Fe- and Pb-bearing residues are fumed in a DC arc furnace, obtaining in one example a final slag with 43% FeO, 24% SiO₂, 13% CaO, 6% MgO and 5% Al₂O₃.

- 15 The smelting processes in above mentioned prior art documents take place in a packed bed or a still bath configuration, and not in an agitated bath or flash smelter at temperatures around 1300 °C.

20 Recent literature mentions high temperature treatment of Zn-containing Fe-based secondary residues, such as EAF dusts. These temperatures are indeed needed to ensure a high Zn-fuming rate, down to low Zn content in the slag, in one single operation. In a known bath or flash smelting processes, the hitherto commonly used fayalite type of slag (2FeO.SiO₂) is heated to well above its melting point (of about 1100 °C) during the metallurgical operation. Such strong
25 superheating of the slag significantly shortens the lifetime of the refractory lining of the vessel. Using a water-cooled lining counters this effect, but at the prize of greatly increased heat losses. The batchwise operations in these smelters are therefore intentionally
30 operated at low temperatures in order to preserve the bath lining and to limit the energy consumption; this however results in a discontinuous and slow fuming.

The primary aim of the invention is to provide a process for high-
35 rate Zn-fuming, avoiding the corrosion of the vessel lining and limiting heat losses to a reasonable value.

To this end, a process is described, which combines forced agitation with a specially formulated freeze-lining slag. By agitation it is
40 understood that, whether in the gas phase or in the liquid phase, the reacting compounds are forcefully intermixed with means that go beyond natural convection, such as e.g. with lances, tuyeres, plasma torches or other high momentum injection techniques.

Another object of the invention concerns a so-called submerged plasma torch furnace, which is particularly suitable for implementing the invented Zn-fuming process.

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The invented process for the valorisation of metal values in a Zn-, Fe- and Pb-bearing residue, comprises the steps of:

- subjecting the residue to a flash or agitated bath fuming step, thereby producing an Fe-bearing slag and Zn- and Pb-bearing fumes;
- 10 and
- extracting the Zn- and Pb-bearing fumes and valorising Zn and Pb; characterised in that CaO, SiO₂ and MgO are added as a flux before or during the fuming step so as to obtain a final slag composition with:

$$\frac{[\text{Fe}]}{[\text{SiO}_2]} + \frac{[\text{CaO}]}{[\text{SiO}_2]} + \frac{[\text{MgO}]}{3} > 3.5;$$

$$0.1 < \frac{[\text{CaO}]}{[\text{SiO}_2]} < 1.3; \text{ and}$$

$$6 < [\text{SiO}_2] < 22,$$

- 15 all concentrations being expressed in wt%.

By combining the use of agitated bath or flash smelting processes with especially adapted freeze-lining slag compositions, which do not need superheating at the process temperature, a rapid fuming process

20 is obtained that can be run continuously. The slag readily forms a protective crust on the refractory lining of the vessel, thereby providing adequate thermal insulation. Also, the yield of the invented process is highly increased compared to prior art processes. The process is particularly suited for treating neutral leach residue

25 or weak acid leach residue.

Dolomite and/or limestone are advantageously used as the sole sources for flux additions. The concentration of MgO in the final slag is preferably less than 5 wt%.

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If Cu is present, a matte or alloy phase is produced in the fuming step, which contains a significant part of the Cu and a significant part of the precious metals. The term significant is, in this context, to be understood as corresponding to a recovery of at least

35 30 wt.% of the individual metals.

If Ge is present, the major part of it is fumed together with Zn and Pb. It can then be separated from the fumes, e.g. by co-precipitation

with Fe hydroxide or by addition of tannic acid. Other useful separation techniques are solvent extraction and the use of ion-exchange resins.

5 The fuming process can be performed in reactors such as a plasma flash furnace and a submerged lance furnace. A single-chamber submerged plasma reactor comprising one or more plasma tuyeres as heat, gas and momentum sources, the tuyeres being arranged such that the plasma is generated under the surface of the molten
10 slag phase, constitutes a novel concept in the art of Zn-fuming, and is particularly well suited for implementing the invented process, because of the high energy production coupled to a small quantity of generated gases. This reactor can be equipped with water-cooled peripheral walls, and can be operated in a continuous manner.

15 The details of the invention are now discussed.

The fuming step consists in the reduction-smelting of the residue, whereby reductants such as natural gas, LPG, coal or cokes, and
20 possibly fluxes such as limestone (CaCO_3) dolomite (MgCO_3 , CaCO_3) and silica (SiO_2) are added to produce a fast fuming slag with a high melting point. This high melting point corresponds to limited superheating of the slag. This greatly facilitates freeze-lining, i.e. the formation of a crust on the inner surface of the cooled
25 vessel walls. Limited superheating results in the formation of a relatively stable and thick crust, ensuring good thermal insulation and efficiently protecting the vessel lining from corrosion. Heat losses towards the cooled walls are thus greatly reduced. Moreover, the relatively low silica content of the slag appears to enhance the
30 fuming rate. A slag melting point of at least 1250 °C, and preferably of at least 1300 °C is recommended.

Figure 1 illustrates slag compositions on a ternary CaO-FeO-SiO₂ phase diagram. Representative prior art fayalite slags are shown as areas
35 under references 1, 2 and 3. See "Phase Equilibria and Thermodynamics of Zinc Fuming Slags", E. Jak and P. Hayes, Canadian Metallurgical Quarterly, vol 41, No 2, pp 163 - 174, 2002. The slag composition according to this invention are shown as areas under reference 4 (for 0 wt% MgO) and references 4 + 5 (for 5 wt.% MgO).

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In most cases, the Zn-bearing residue can be fluxed according to the above criteria using limestone and/or dolomite only. Minimising the

addition of silica results in a slag having the required high melting point and a fast fuming kinetics. The effect of MgO is to further increase the melting point of the slag. Due to its relatively high cost, it is recommended to limit the concentration of MgO in the final slag to 5 wt.%.
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In the fuming process, Zn and Pb are concentrated in the fumes. Cu is collected in a separate matte phase. Through leaching of these fumes, Zn and Pb can be separated in a Pb-containing residue and a Zn-containing leaching liquor. If the Zn-, Fe- and Pb-bearing residue also contains Ge, the Ge present in the fumes may be separated and treated batch-wise in a subsequent, Ge-rich fuming campaign. The Ge separation from the fumes is preferably performed by leaching, followed by co-precipitation with Fe hydroxide or by addition of tannic acid. The same principles apply for In.
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The reactor types mentioned before lend themselves to large-scale, single-vessel operations. The overall process is compact, uses a single smelting/fuming reactor at high temperature and ensures a high metal value recovery while producing environmentally acceptable end products. The invention thus provides for an essentially waste-free process, which can compete economically with hydro-metallurgical Zn residue treatments. The slag is an environmentally acceptable output for Fe, which can be upgraded as gravel substitute in concrete. The actual valorisation of metallic Fe is unimportant due to its relatively low concentration in the contemplated residues and to its rather low intrinsic value.
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A single-chamber reactor equipped with submerged plasma fired tuyeres has been specially designed for use in the above-described process. During start-up, the reactor is filled with slag, which is molten down by the plasma tuyeres until these are submerged. Then, a Zn-bearing residue is added, without the need for any special feed preparation, like drying or comminuting. The energy provided by the plasma tuyeres results in the melting of the feed and in the fuming of valuable metals like Zn, Pb, Ge and In. The reductants can be fed through the tuyeres (natural gas, LPG) or added to the feed (coal, cokes). The tuyeres are preferably submerged at a depth allowing them to contact the slag phase only, as the slag has a lower corrosive nature than the heavier other phases.
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The use of the invented slag composition is preferably combined with water-cooling of the reactor's periphery: water-cooling of the side

walls facilitates freeze-lining, which has, as explained above, a particularly advantageous effect.

Advantages of this furnace over the submerged lance furnace mainly stem from the use of electricity as a heat source. The submerged plasma reactor indeed achieves high flexibility through its ability to operate in a wide range of oxygen potentials, while minimising the total amount of off-gasses produced. Reduced off-gas amounts allow for a compact installation, operating with low emission of environmentally harmful gasses such as CO_2 . Unlike a plasma flash furnace, where the molten phases settle without any agitation, the submerged plasma induces a suitable level of bath agitation, which lead to greatly accelerated reduction kinetics and which allows humid or wet materials to be directly fed into the furnace.

The following example illustrates the separation of different non-ferrous metals contained in a roasted and subsequently leached blende residue.

1500 kg of weak acid leach residue, which mainly consists of zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$), lead sulphate (PbSO_4), calcium sulphate (CaSO_4), zinc sulphate (ZnSO_4) and impurities like CaO , SiO_2 , MgO , Al_2O_3 , Ag , Cu and Ge , are dried and thoroughly mixed with 150 kg of cokes, having a purity of more than 85 % C. The feed is fluxed with 90 kg of dolomite and 60 kg of limestone.

The mixture is then injected through a tuyere attached to a 1 MW air plasma torch for flash fuming at a feed rate of 12 kg/min. The furnace walls are water-cooled and protected by a thin layer of refractory at start-up. After two hours of smelting, the slag is tapped. The recovered fumes are rich in Zn and Pb , which are present as ZnO , PbO and/or PbSO_4 .

The slag is tapped at 1325 °C with only limited superheating thanks to the fluxing of the feed resulting in a final slag composition according to the invention. Next to the slag and fumes, a separate Cu containing matte was tapped.

The analysis of the different feeds and productions is given in Table 1, together with the metal distribution across phases. "Others" refers to impurities and to bound elements such as oxygen. For the cokes, "Others" refers to ash content; for the fluxes, to impurities such as Al_2O_3 .

Table 1: Material balance and metal distribution across phases

| Feed to fuming furnace | | | | | | | | | | | | | |
|------------------------|-----------|--------------------|------|------|------|------|------|------------------|------|------|------|------|--------|
| Component | Mass (kg) | Composition (wt.%) | | | | | | | | | | | |
| | | Ag | Pb | Cu | Zn | Fe | CaO | SiO ₂ | MgO | S | Ge | C | Others |
| Residue | 1200 | 0.06 | 4.72 | 2.40 | 23.8 | 19.0 | 2.98 | 7.15 | 0.71 | 5.90 | .008 | | 33.3 |
| Limestone | 60 | 0.00 | 0.12 | 0.10 | | 3.00 | 50.4 | 6.10 | 0.46 | | | 10.9 | 28.9 |
| Dolomite | 90 | | 0.00 | 0.00 | 0.02 | 0.33 | 32.0 | 0.60 | 20.0 | | | 12.8 | 34.2 |
| Cokes | 150 | | | | | | | | | | | >85 | <15 |
| Total feed | 1500 | 0.05 | 3.78 | 1.92 | 19.0 | 15.3 | 6.32 | 6.00 | 1.79 | 4.72 | 0.01 | 9.71 | 31.3 |

| Products of the process | | | | | | | | | | | | | |
|-------------------------|-----------|--------------------|------|------|------|------|------|------------------|------|------|-------|---|--------|
| Component | Mass (kg) | Composition (wt.%) | | | | | | | | | | | |
| | | Ag | Pb | Cu | Zn | Fe | CaO | SiO ₂ | MgO | S | Ge | C | Others |
| Fe-slag | 500 | 0.00 | 0.01 | 0.45 | 2.47 | 20.9 | 16.8 | 16.6 | 4.93 | 2.23 | <.001 | | 35.7 |
| Matte | 175 | 0.18 | 0.09 | 8.38 | 3.39 | 56.4 | 3.11 | 0.91 | 0.46 | 16.6 | .008 | | 10.4 |
| Fumes | 500 | 0.08 | 11.3 | 2.39 | 53.5 | 5.39 | 1.10 | 1.10 | 0.27 | 6.12 | .016 | | 18.8 |

| Distribution (%) | | | | | | | | | | | | |
|------------------|-----------------|----|-----|----|----|----|-----|------------------|-----|----|----|--|
| Component | Fraction (wt.%) | Ag | Pb | Cu | Zn | Fe | CaO | SiO ₂ | MgO | S | Ge | |
| Fe-slag | 33 | | | 8 | 4 | 48 | 88 | 92 | 92 | 10 | | |
| Matte | 12 | 47 | | 51 | 2 | 43 | 6 | 2 | 3 | 35 | 15 | |
| Fumes | 33 | 53 | 100 | 42 | 94 | 8 | 6 | 6 | 5 | 55 | 85 | |

The slag analysis shows minimal amounts of leachable heavy metals, such as Pb, ensuring that the slag is environmentally clean. The high percentage of "Others" in the slag is attributable to oxygen bound to the metals.

The environmental stability of the slag was tested on the slag as such and after formation of concrete containing 30% slag and 10% cement. The tests were performed according to European norm NEN 7343, whereby the material is broken to less than 4 mm and percolated with acidified water. The leachability was assessed according to the Flemish VLAREA ("Vlaams reglement voor afvalvoorkoming en -beheer") norm for non-ferro metallurgical slags. The leachability of both the slag and the slag-containing concrete proved to be well below the limits applicable to products intended for the building industry.

The invented process thus achieves the separation of the metals as follows:

- Zn, Pb and Ge in the fumes, which can be treated by known means for separation of Pb and Ge in different residues, and of Zn in a leach liquor;

- Cu and precious metals in a matte or alloy, which can be refined using a classical Cu and precious metals flowsheet;
- Fe in an inert, environmentally clean slag, reusable as e.g. gravel substitute in concrete.